

Note

Degree of substitution of cellulose derivatives containing n different substituent groups*

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Rigorous calculation of degree of substitution (d.s.) for cellulose derivatives containing only one kind of substituent has been well worked out and reported by a number of workers¹⁻⁴. For cellulose derivatives containing two different substituent groups, the d.s. has usually been estimated from the d.s. calculated by disregarding the second substituent. However, a rigorous calculation has been made for the case where there are two independently measurable substituents⁵.

During our calculation of the rigorous equation for the d.s. of three substituents, a general equation was developed that permits calculation of the d.s. of any substituent group in a modified polysaccharide having any number, n , of independently measurable, substituent types.

Derivation of the equation begins with the definition of the analyzable property in terms of d.s. and the "molecular weight" of the components:

$$\frac{PC_1}{100} = \frac{(d.s._1)(MW_1)(N_1)}{(MWU) + (d.s._1)(MWG_1) + (d.s._2)(MWG_2) + \dots} \quad (I),$$

where PC_1 is the weight percent of measurable component in substituent group 1; MW_1 is the molecular weight of the measured component, N_1 is the number of measurable components in the substituent group, MWG_1 is the molecular weight added for each substituent group, and MWU is the molecular weight of the basic repeating-unit, the glucosyl residue. For example, for the partially hydrolyzed derivative of the cellulose-acrylamide addition-reaction, a product that contains *O*-(carbamoyl ethyl) and *O*-(carboxyethyl) groups, PC_1 is the percentage of nitrogen; MW_1 is 14.008, the atomic weight of nitrogen; N_1 is 1 (there is one nitrogen atom in each

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carbamoylethyl group); MWG_1 is 71.08, the weight added per carbamoylethyl group; MWG_2 is 72.06, the weight added per carboxyethyl group; and MWU is 162.14, the weight of the glucosyl residue. A similar equation is developed for the analyzable component of each substituent group. For example, in the foregoing case, PC_2 is the percentage of carboxyl and MW_2 is 45.02, the equivalent weight of a carboxyl group. These basic-definition equations are solved for d.s. in terms of the analyzable component.

This same basic definition was used by Horton and Pardoe⁶. In their work, the equation was not solved directly but rather a computer was used to calculate and test the percent of analyzable component for all d.s. values and then those values fitting the experimental data were printed out. Their method may be used for any number of substituents, but it must have a computer.

Our general solution began by solving the definition equations for the various cases of multiple constituents. After solution of the equations for four substituents, the general equation was induced from the repeating format. The following series of equations shows the pattern.

For two substituents the equation is:

$$d.s._1 = \frac{(PC_1)(MWU)(MW_2)(N_2)}{(100)(MW_1)(N_1)(MW_2)(N_2) - (MW_2)(N_2)(PC_1)(MWG_1) - (MW_1)(N_1)(PC_2)(MWG_2)} \quad (2)$$

For three substituents it becomes:

$$d.s._1 = \frac{(PC_1)(MWU)(MW_2)(N_2)(MW_3)(N_3)}{(100)(MW_1)(N_1)(MW_2)(N_2)(MW_3)(N_3) - (MW_2)(N_2)(MW_3)(N_3)(PC_1)(MWG_1) - (MW_3)(N_3)(MW_1)(N_1)(PC_2)(MWG_2) - (MW_1)(N_1)(MW_2)(N_2)(PC_3)(MWG_3)} \quad (3)$$

or, in a rewritten form,

$$d.s._1 = \frac{\frac{(PC_1)(MWU)}{(MW_1)(N_1)}}{100 - \frac{(PC_1)(MWG_1)}{(MW_1)(N_1)} - \frac{(PC_2)(MWG_2)}{(MW_2)(N_2)} - \frac{(PC_3)(MWG_3)}{(MW_3)(N_3)}}$$

The general form of the equation then becomes:

$$d.s._j = \frac{\frac{(PC_j)(MWU)}{(MW_j)(N_j)}}{100 - \sum_{i=1}^n \frac{(PC_i)(MWG_i)}{(MW_i)(N_i)}}$$

This equation is, in fact, a statement of d.s. as a ratio of moles of substituent group per glucosyl residue.

There are three ways that the equations can be used. The first is simply to substitute the analytical data into the equation and calculate the d.s. The second is to use the equation to generate a table of d.s. values of each substituent with in-

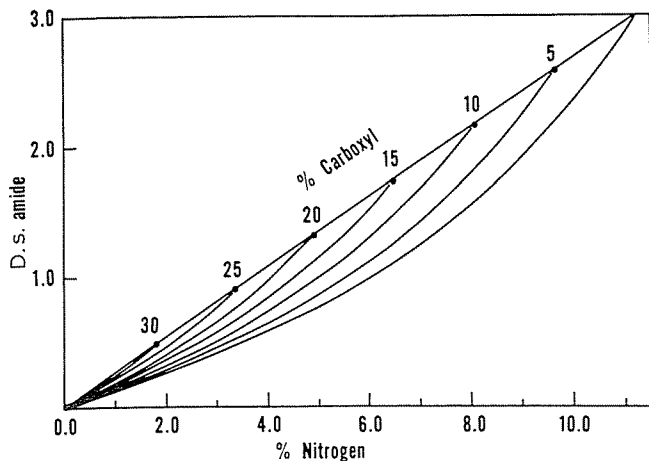


Fig. 1. D.S. by amide vs. percent of nitrogen at various percentages of carboxyl group for *O*-(carbamoylethyl)-*O*-(carboxyethyl)cellulose.

creasing percentages of analyzable components. Here, a computer is highly useful for calculation of all possible combinations. The tables do become cumbersome as the number of substituents increases, or as the analytical increment is made smaller. The third, graphic method, although applicable to at most two substituents, is the quickest and easiest for a large number of determinations. In it, d.s. is plotted against the percent of analyzable component to give a curve or, for two substituents, a family of curves. The example in Fig. 1 shows the curves for d.s. by amide at a series of carboxyl values (%) for *O*-(carbamoylethyl)-*O*-(carboxyethyl)cellulose. There is a corresponding plot for d.s. by carboxyethyl.

The equation may be applied to essentially any polymer made up of modifiable repeating-units. For example, poly(vinyl alcohol) may be considered as a polymer having a unit weight of 44.05 and a maximum d.s. of 1.0. Another example would be an acrylamide-acrylic acid copolymer in which the acrylic acid unit may be considered as the basic repeating unit and the weight added per modified (amide) group is actually -1. A form of the equation may be used to calculate the fraction of modification wherever a portion of repeating units is modified and all of the modifying group can be determined analytically.

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